Evaluation of indoor pollutant emissions from portable air cleaners

Hugo Destaillats

Lawrence Berkeley National Laboratory

Environmental Energy Technologies Division, Indoor Environment Group

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Why portable air cleaners?

- A **diverse set** of devices is available in a **growing market**
- There is **limited prior research, standards or regulations** on pollutant emissions from portable air cleaners
- There is **little information on emissions and effectiveness**
- In some cases, **marketing claims** on IAQ benefits **seem overstated**
- **Poorly engineered devices may pose risks** by emitting ozone, volatile organic compounds (VOCs), particulate matter (PM) and/or reactive oxygen species (ROS)
- Previous studies showed formaldehyde emissions

The objectives of this study are…

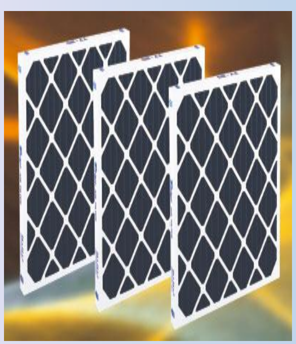
- Evaluate the **primary and secondary emissions** of indoor air pollutants
- Evaluate the devices' pollutant **removal efficiencies**
- Emphasize a **new generation of equipment, emerging technologies**

commonly used in air cleaning

filtration

HEPA filters

adsorption



Activated carbon

chemisorption

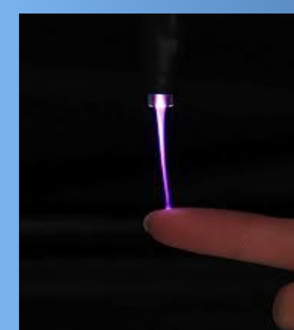
Permanganate + zeolites

newer technologies

photocatalysis

UV light + TiO_2

non-thermal plasma



Electron jet, discharge, arc

microbial thermal inactivation

Ceramics

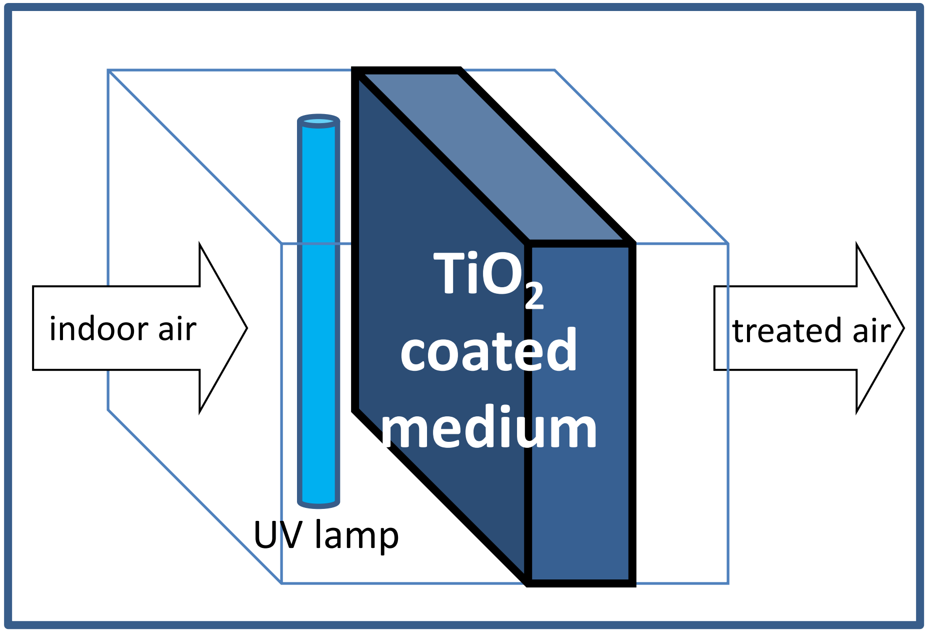
Project Tasks

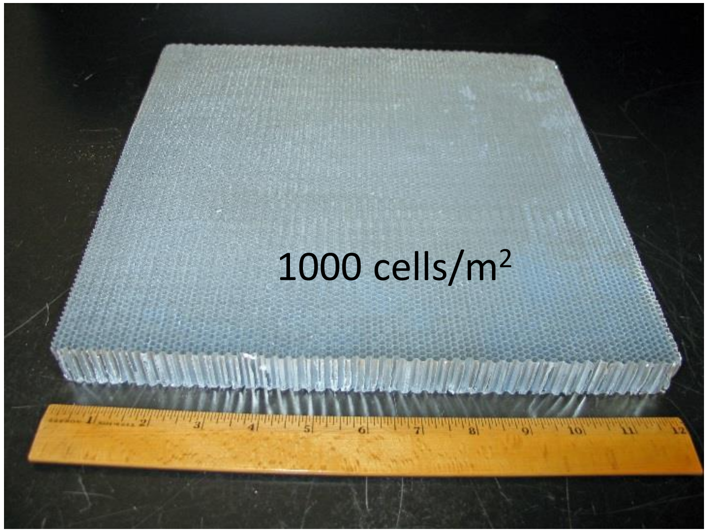
- Selection and procurement of air cleaners to be studied
    - Photocatalytic oxidation (PCO), non-thermal plasma and microbial inactivation using heated ceramics
    - Designed for room-size application
    - 6 devices purchased from on-line retailers, manufacturers
- Development of a laboratory test protocol
    - Existing methods (VOCs, PM, ozone)
    - Developed a new method to quantify ROS
- Characterization of emissions from air cleaners
    - Systematic evaluation of each of the 6 air cleaners
- Evaluation of the impacts of air cleaners on indoor air quality
    - Determined primary and secondary emission rates
    - Determined pollutant removal efficiencies
    - Predicted impact on exposure

Outline of methods and results

- Description of air cleaners
- Laboratory methods
- Representative experimental results
- Modeled results
- Discussion and implications

Photocatalytic oxidation (PCO) air cleaners



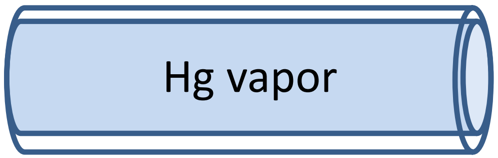


Example of catalyst-coated medium: honeycomb monolith

1. TiO_2 is excited with UV lamp(s) — (design/dimensioning constraints)
2. Volatile Organic Compounds (VOCs) adsorbed on TiO_2 surface — (design/dimensioning and physical-chemical constraints)
3. VOCs react with photogenerated charges, surface OH & reactive species — (chemical constraints: partially oxidized byproducts)

Different types of UV lamps are used in PCO

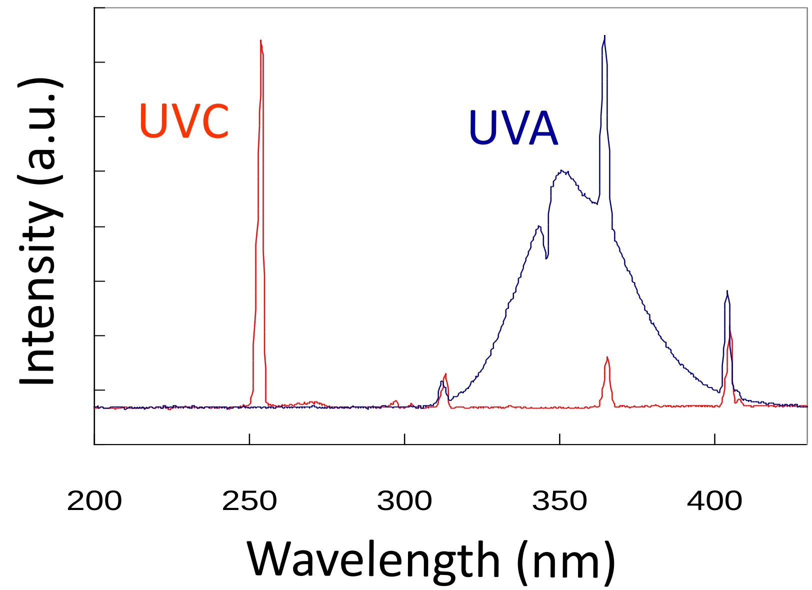
Vacuum UV (VUV)



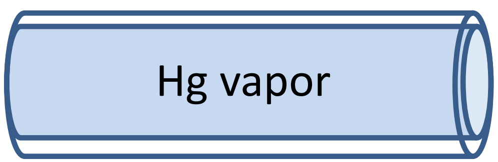
λ_{max} = 185 nm and 254 nm

uncoated quartz

Produces ozone



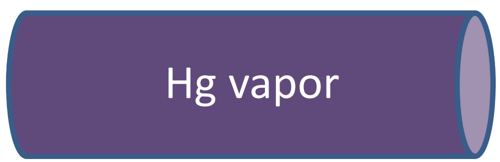
Ozone-free (UVC)



λ_{max} = 254 nm

coated quartz

Black light (UVA)



λ_{max} = 365 nm

coated quartz

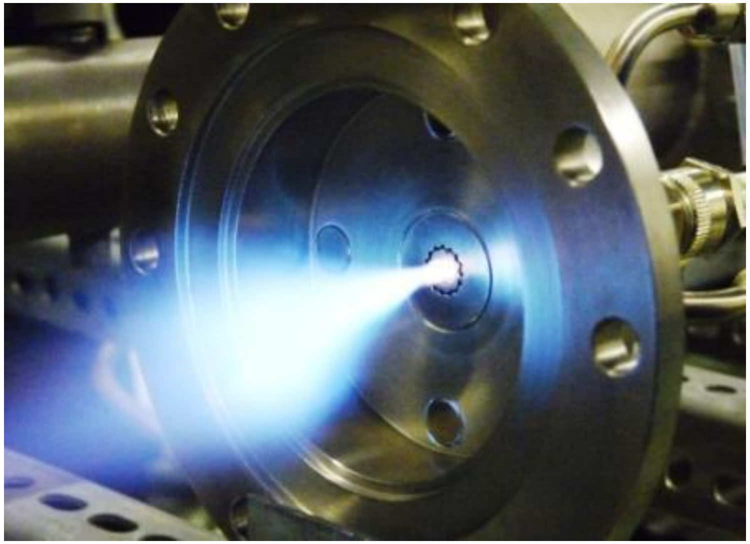
Do not produce ozone

Three PCO air cleaners were tested in this study

	PAC 1	PAC 2	PAC 3
Principle of operation	Photocatalyst (TiO_2) + UVA lamp (365 nm)	Photocatalyst + ozone-free UVC (254 nm) + HEPA filter + “oxygenating catalyst”	Photocatalyst + ozone-generating VUV lamp
Manufactu-rer’s description	Hydroxyl generator. Targets odors, VOCs, microorganisms	Room air purifier. Targets PM, germs, viruses, mold, mildew and VOCs	Residential air purifier and sanitizer. Targets mold, bacteria, viruses, odors, VOCs
Retail price	$ 450	$ 130	$500

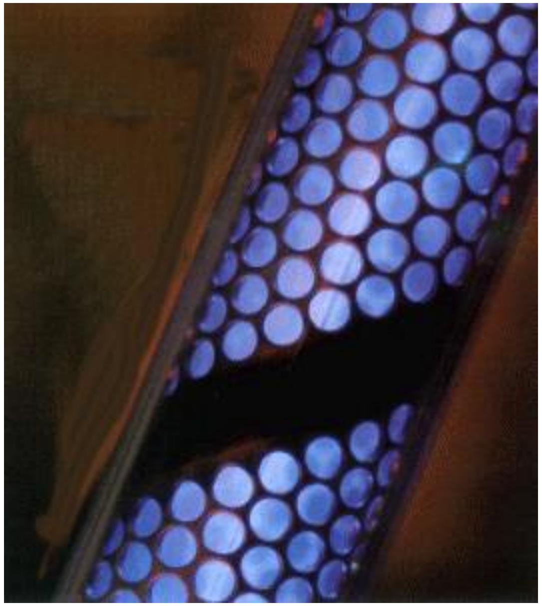
Non-thermal plasma

A non-thermal plasma is a partially ionized gas in which the mean energy of the electrons is considerably higher than that of the ions and bulk gas molecules.



Obtained by exposure to strong electrical field:

- Corona discharge
- Dielectric barrier discharge
- Gliding arc
- Electron beam



Applications:

- Indoor air cleaning
- Treatment of flue gas and industrial effluents
- Antimicrobial / sterilization
- Surface treatments
- Clean combustion
- Analytical instrumentation

Plasma & ceramic heater air cleaners tested in this study

	PAC 4	PAC 5	PAC 6
Principle of operation	Non-thermal plasma with generation of reactive oxygen species	Ceramic room heater with ionizer	Localized high temperatures (400 F) kills microorganisms; does not change room temperature
Manufactu-rer's description	Air purifier. Targets airborne microorganisms	Room air heater with ionizer. Targets dust, pollen, smoke and pet dander.	Air purifier. Targets airborne microorganisms
Retail price	$ 170	$ 95	$ 230

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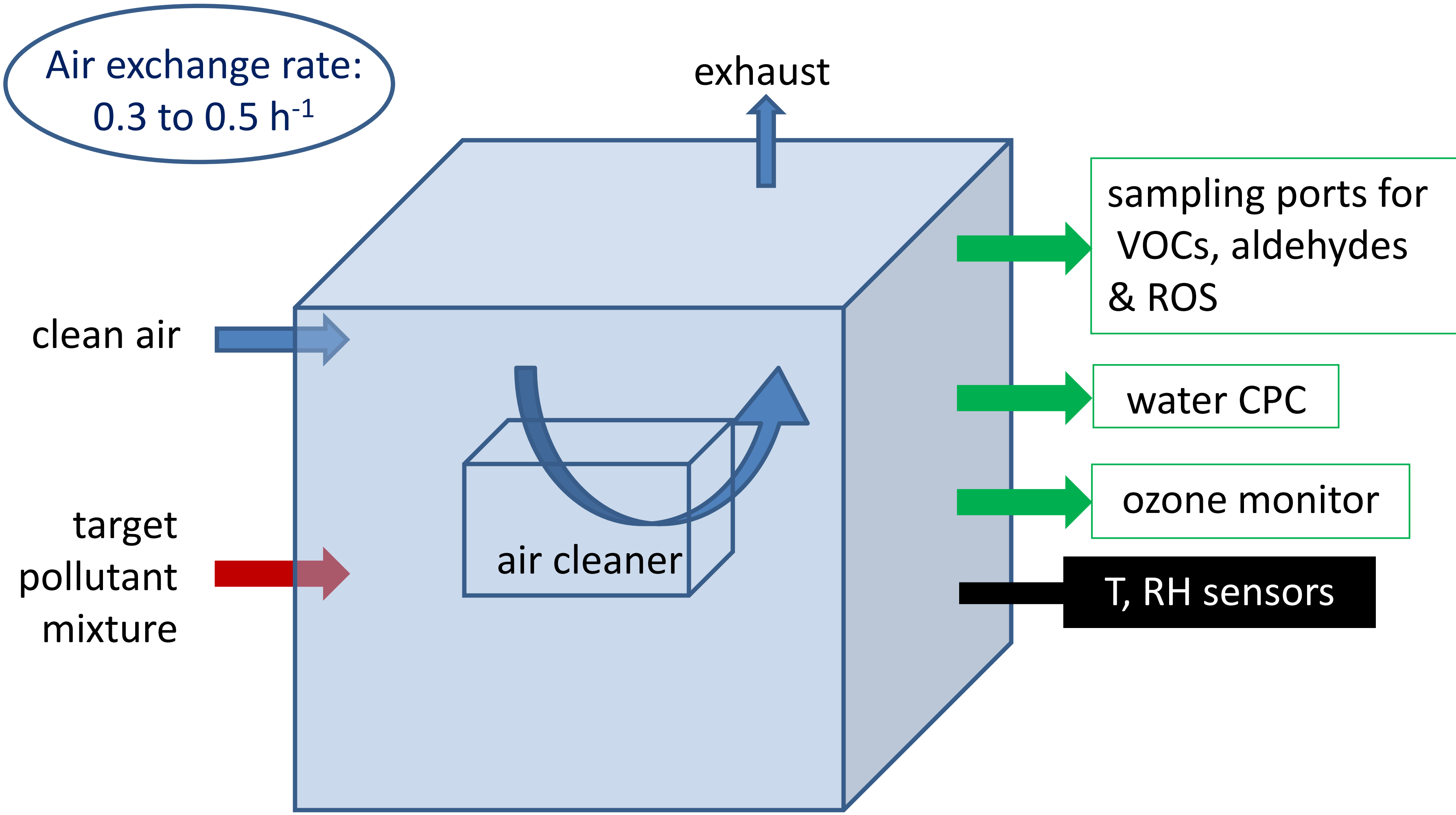
Room-sized chamber setup

well-mixed 20-m³ stainless steel chamber



Sample collection and analytical methods

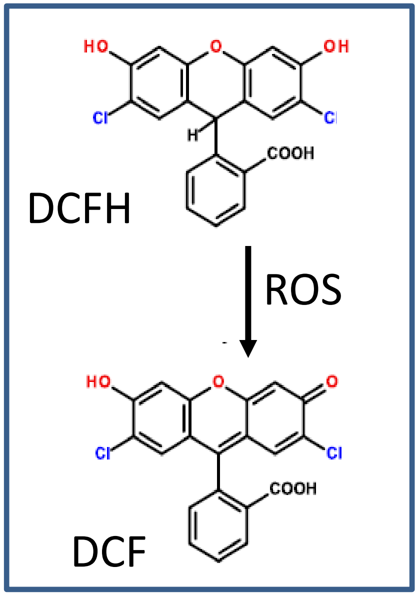
Analyte	Mode	Collection method	Analysis
ozone	real-time	continuous	UV photometric
ultrafine particles (UFP)	real-time	continuous	Water CPC
volatile organic compounds (VOCs)	integrated	sorbent tubes	GC/MS
volatile carbonyls	integrated	DNPH-coated silica	HPLC
reactive oxygen species (ROS)	integrated	fluorescent probes	Fluorimeter

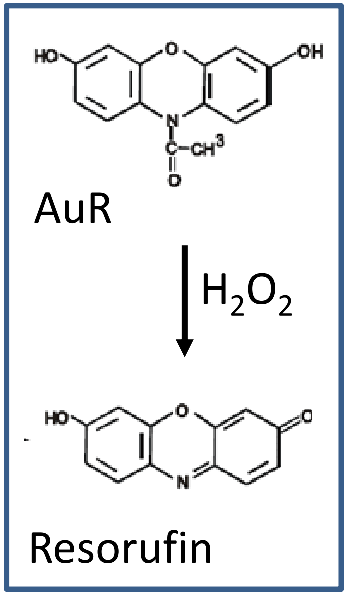
A method was developed to quantify ROS

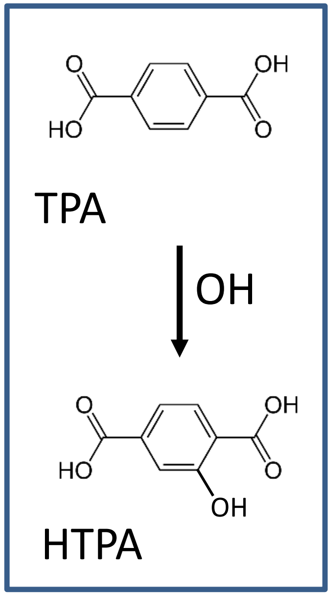
	2',7'-Dichloro fluorescin (DCFH)	Amplex® ultra Red (AuR)	Terephtalic acid (TPA)
ROS detected	H_2O_2, $HO^{\cdot}$, $ROO^{\cdot}$, $O_2^{\cdot-}$	H_2O_2	$OH^{\cdot}$
ROS-induced fluorescent byproduct	2,7-dichloro fluorescein (DCF)	resorufin	2-hydroxy-terephtalate (HTPA)
Excitation / emission (nm)	485 / 530	563 / 587	310 / 412
Reported detection limit	50 nM	50 nM (10 pmoles)	5 nM (100 fmol)

REACTANT

FLUORESCENT BYPRODUCT





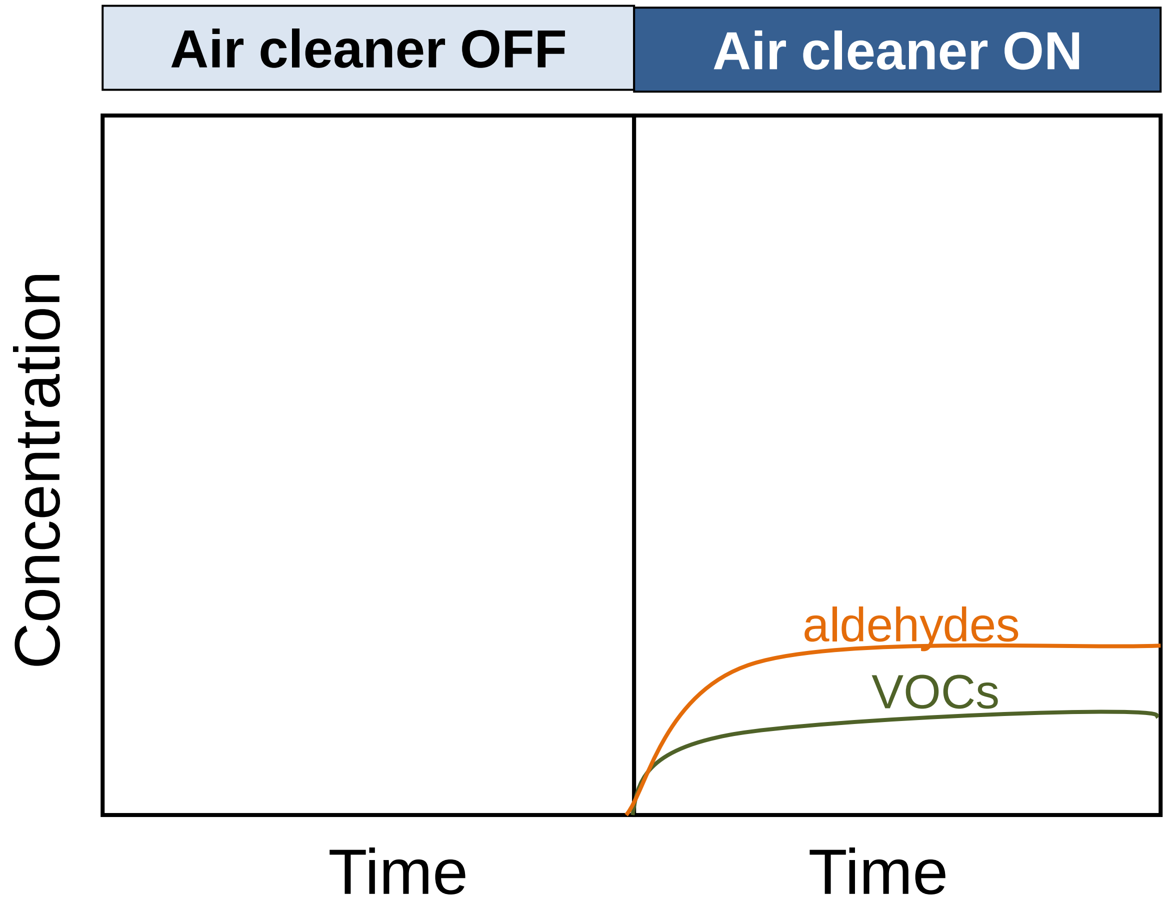


Each air cleaner was tested in two different conditions

PHASE 1: clean air

CHAMBER BACKGROUND

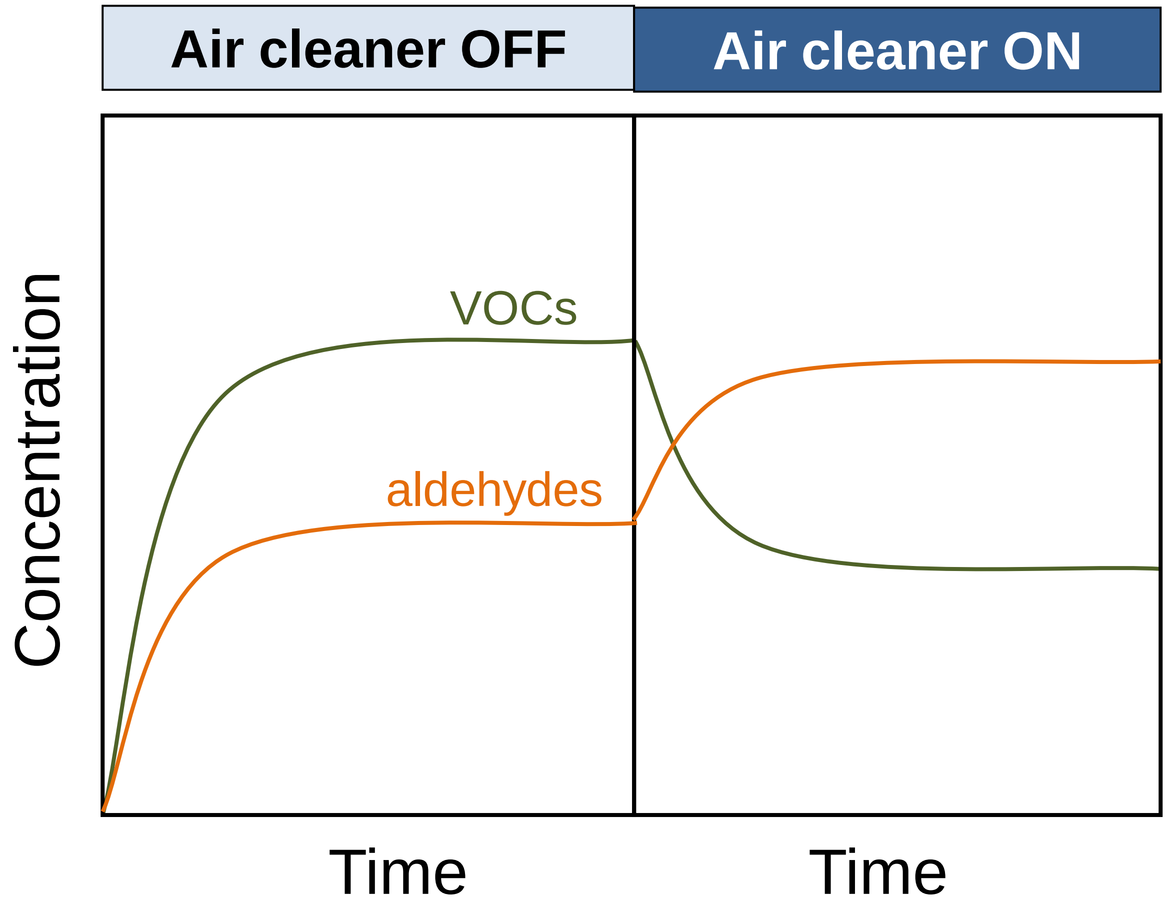
- ~ 2 ppb formaldehyde
- ~1-3 ppb acetone
- ~ 500 #/cm^3 ultrafine particles.



Each air cleaner was tested in two different conditions

PHASE 2: challenge mixture

- formaldehyde
- toluene
- benzene
- styrene
- d-limonene
- pyridine
- trichloroethylene
- butanal
- ethanol
- hexane
- o-xylene
- Total concentration: 150 – 200 ppb



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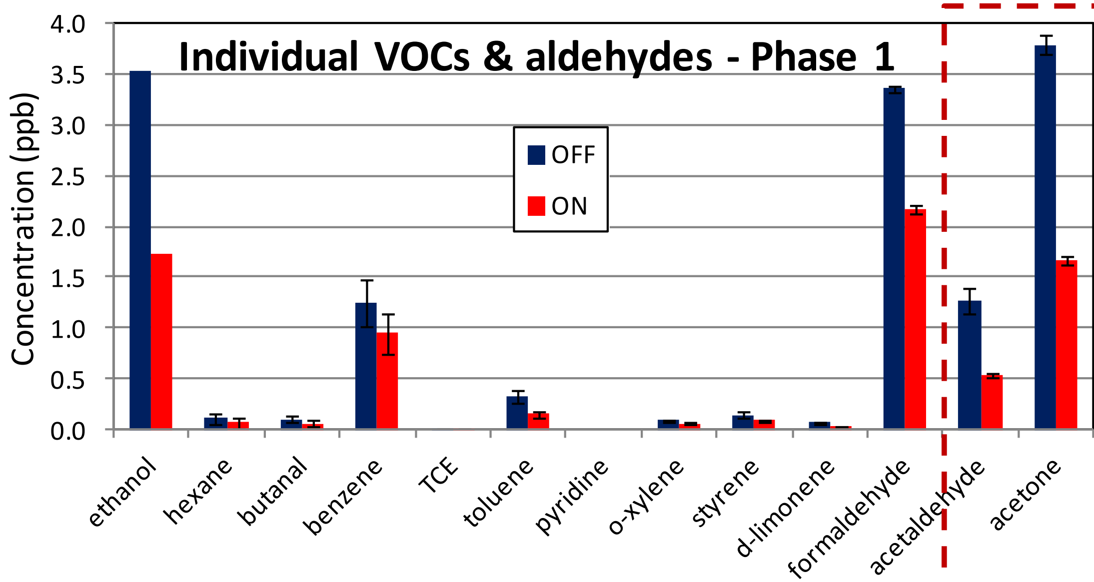
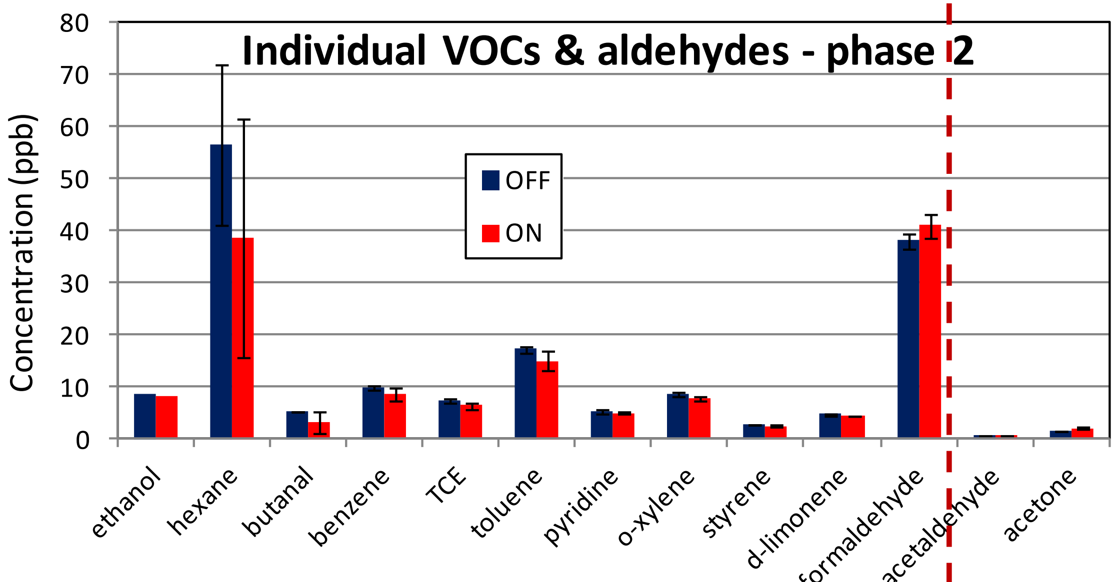
VOC concentrations measured in the chamber

PAC 1



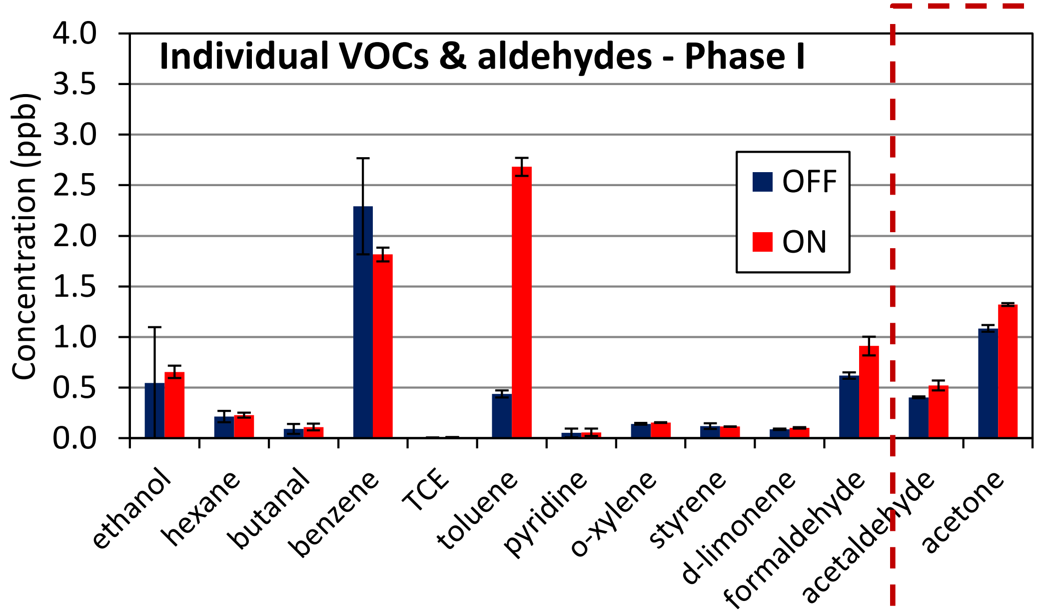


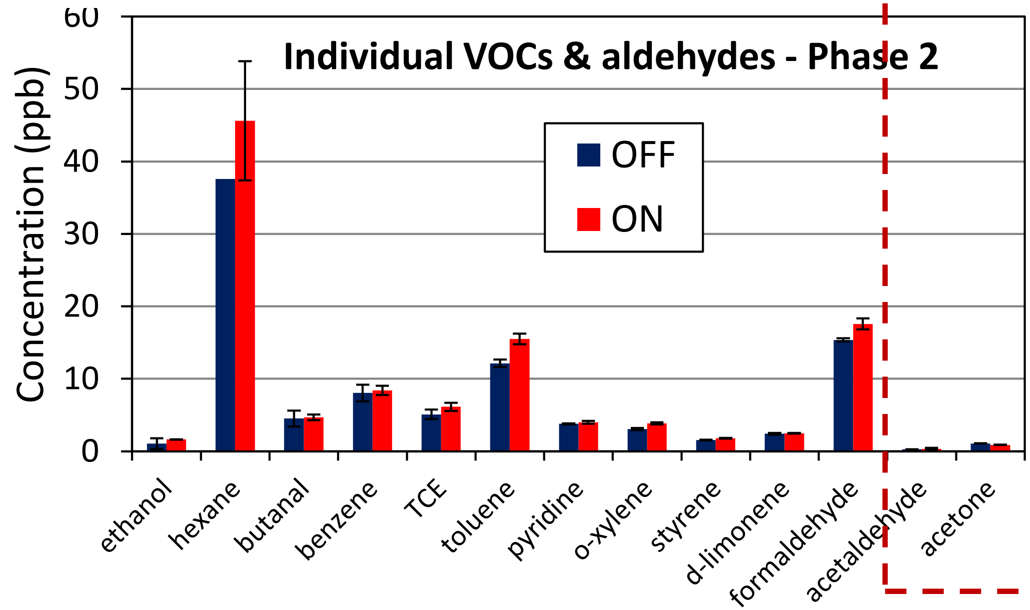
Overall elimination of indoor VOCs

not included in challenge mixture

VOC concentrations measured in the chamber

PAC 2



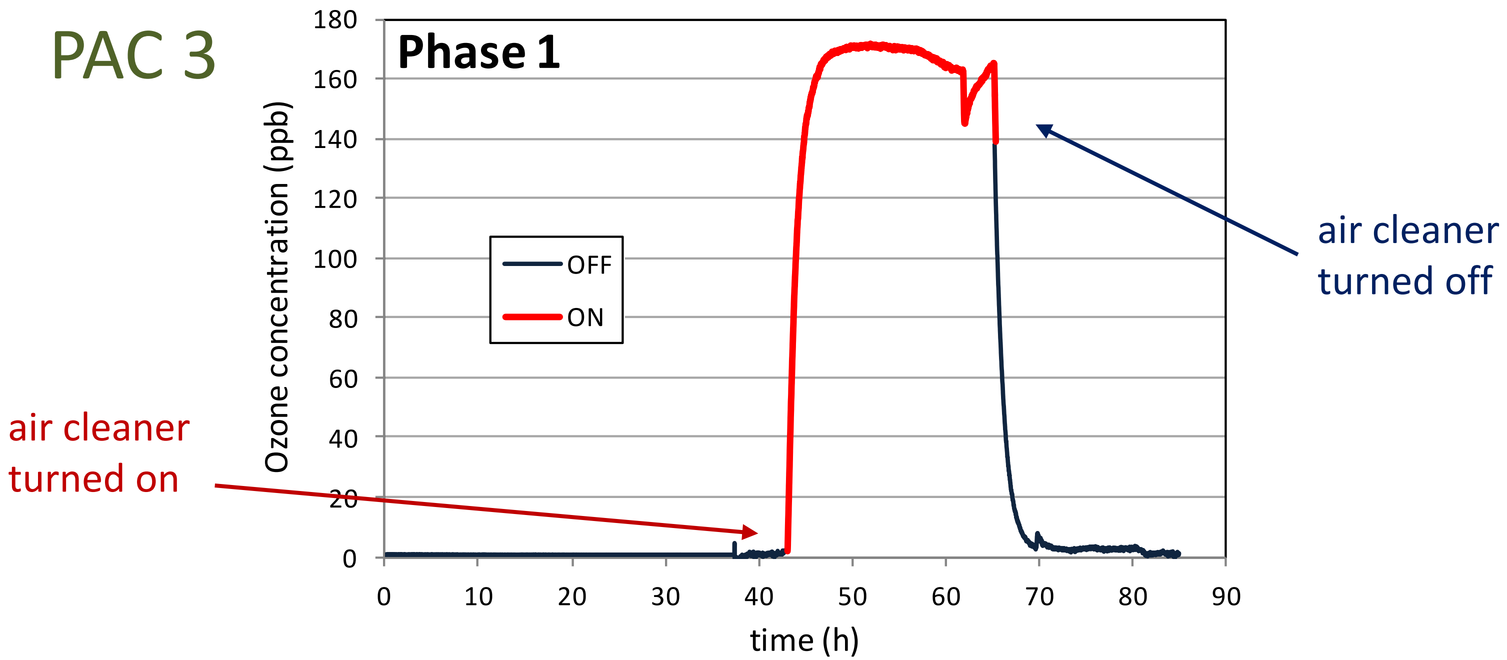


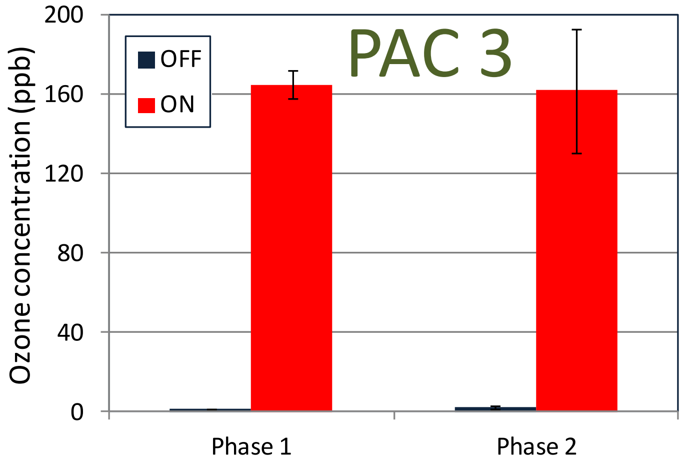
Overall increment of indoor VOCs

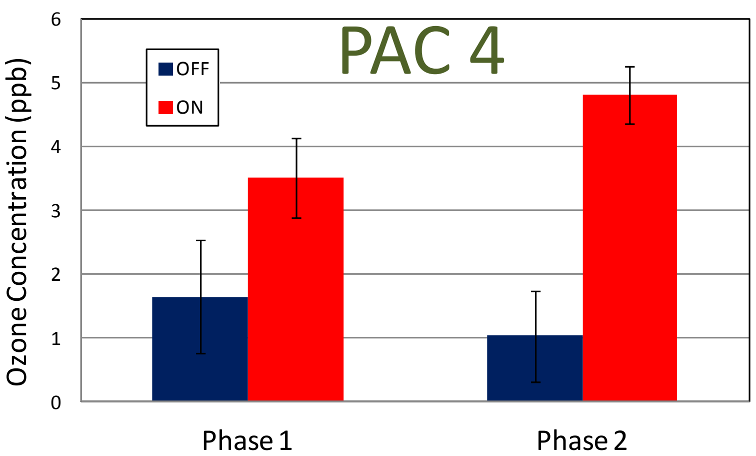
not included in challenge mixture

Ozone measured in the chamber

PAC 3

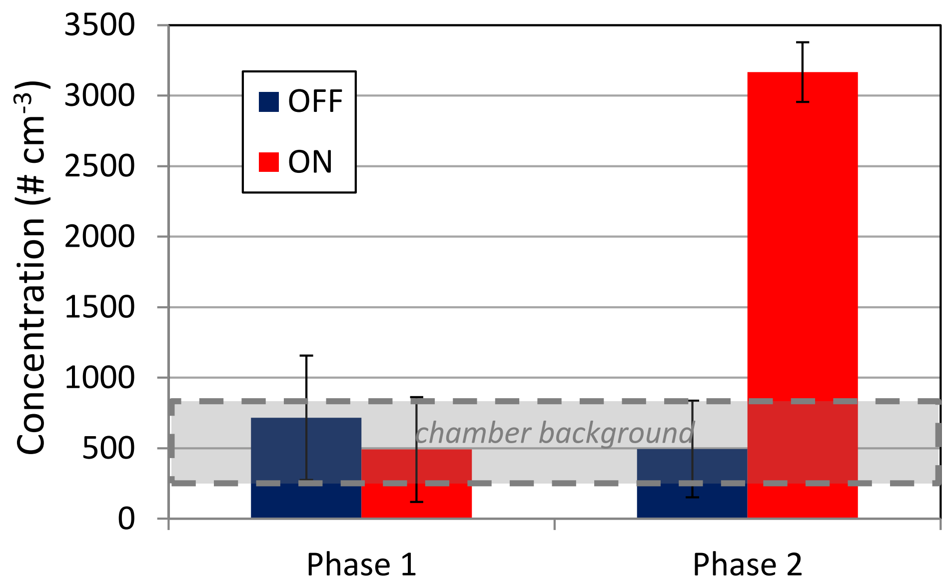


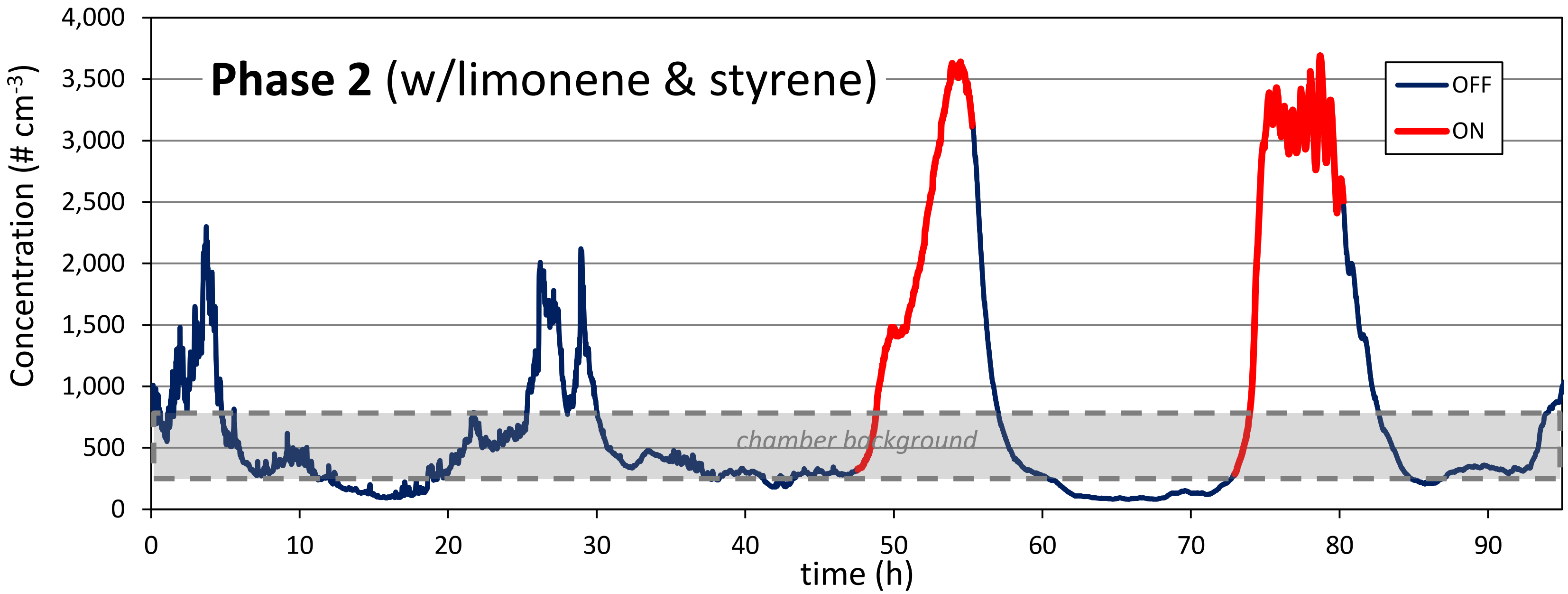




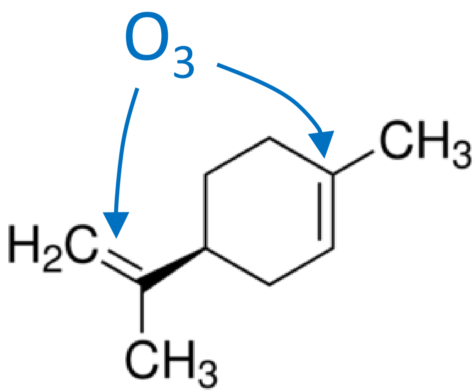
UFP measured in the chamber

PAC 3

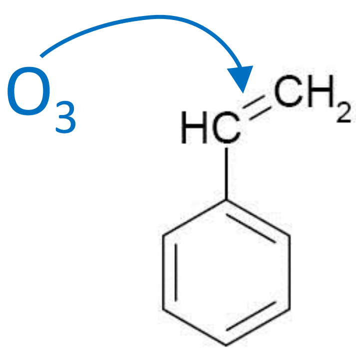




UFP are formed from ozone reactions with alkenes



d-limonene



styrene

- Reactive short-lived species
  (Criegee intermediates)
- UFP yields from ozone reaction with limonene:
  - 10-15 % (Weschler and Shields, 1999)
  - 13 % (Alshawa et al, 2007)
- UFP Yields from reaction with styrene: 3-12 %
  (Na et al, 2006)
- Formaldehyde yield from ozone reaction with:
  - limonene: ~27% (Destaillats et al, 2006)
  - styrene: 37% (Tuazon et al, 1993)
- OH yields from ozone-limonene reactions:
  - 67% (Aschmann et al, 2002)

ROS measured in chamber and at the air cleaner outlet

In the chamber:

below detection limit (Phase 1 & 2)

At the air cleaner outlet:

PAC 4

AuR	**300 ppt**	**$[H_2O_2]^{eq}_{gas}$**
TPA	**47 ppt**	**$[OH]^{eq}_{gas}$**

Main issues:

Measurements requires background correction as a function of ozone concentration, due to contributions of O_3 to the signal.

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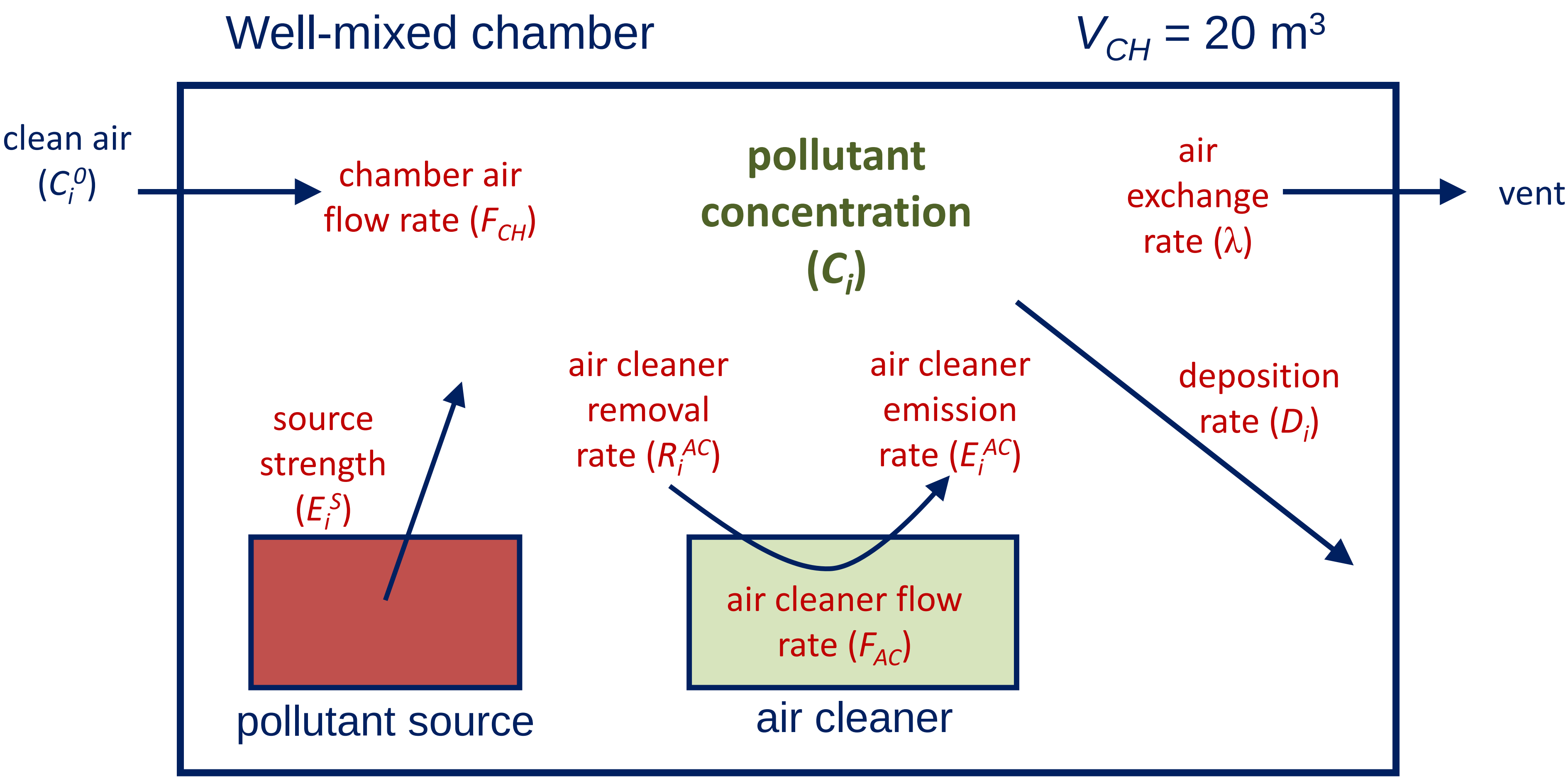
A box model was used to evaluate the impact on IAQ



i = individual pollutant

Pollutant emission and removal rates were calculated

Data corresponding to Phase 2:

	PAC1	PAC2	PAC3	PAC4	PAC5		PAC6
					ionizer	ion + heat	
ozone (mg h^{-1})	-	-	5.9	0.18	-	-	-
UFPs (# particles h^{-1})	-	6.0E+09	3.10E+10	4.9E+09	-	-	-
VOCs (μg h^{-1})							
ethanol	-	16	5.4	539	215	7.4	11
hexane	582	N/A	116	409	398	202	97
butanal	30	-	23	23		62	30
benzene	34	13	38	99	40	42	25
TCE	47	65	74	122	49	37	29
toluene	79	147	171	267	96	173	61
pyridine	10	-	66	90	19	45	136
o-xylene	37	40	91	63	71	176	163
styrene	7.0	12	133	23	41	134	52
d-limonene	8.3	-	273	21	111	605	39
formaldehyde	33	31	36	25	49	229	12
acetone	*9*	*5.0*	*86*	-		*89*	-
benzaldehyde	-	-	*111*	-			-
TOTAL VOCs (μg h^{-1})	792	319	829	1629	992	1343	634
% chamber VOCs	-14 %	+15 %	-28 %	-29 %	+12 %	+19 %	-8 %

Red: emitted **Black:** removed

The removal efficiency was estimated with a simple model

measured

OVERALL EFFICIENCY:
The chamber **concentration reduction factor** is defined as:

$$\omega_i = \frac{\left(C_i^{OFF} - C_i^{ON}\right)}{C_i^{OFF}}$$

CAPACITY:
The **recycle ratio** is defined as:

$$\rho = \frac{\text{airflow through air cleaner}}{\text{airflow through chamber}} = \frac{F_{AC}}{F_{CH}} = \frac{F_{AC}}{\lambda \cdot V}$$

INTRINSIC EFFICIENCY:
The **single pass removal efficiency** at steady-state (*ss*) is defined as:

$$\phi_i^{\rho,ss} = \frac{\left(C_i^{upstream} - C_i^{downstream}\right)}{C_i^{upstream}}$$

These parameters are related by a simple **correlation:**

$$\omega_i = 1 - \left(\frac{1}{1 + \rho \cdot \phi_i^{\rho,ss}}\right)$$

Evaluation of the pollutant removal efficiency

- VOC removal efficiency:
  - evaluated for four devices: PAC1, PAC3, PAC4, PAC6
  - **chamber reduction factors** for individual VOCs were between **0 and 40%**
  - **recycle ratios** were between **0.4 and 1.7**
  - estimated **single-pass efficiencies** for individual VOCs were between **0 and 90%**
  - **styrene and limonene** were reduced by **>97%** with PAC3 (O_3 chemistry)

- UFP removal efficiency:
  - evaluated for two devices: PAC2 (recycle ratio: 1.8) and PAC4 (recycle ratio: 0.7)
  - **PAC2** removed **80-90%** of particles (HEPA filtration)
  - **PAC4** (plasma) removed **35-50%** of particles, above the predictions of the simple model, suggesting that ions or radicals emitted to indoor air adhere to particles and accelerate their deposition

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Predicted impacts on indoor air quality (IAQ) (i/iii)

We calculated contributions to indoor concentration (ΔC) in two model scenarios:

	Indoor air volume, V (m^3)	S/V ratio (m^{-1})	Air exchange rate (h^{-1})	Number of devices (N)
LBNL chamber	20	2.2	0.3 to 0.5	1
Scenario #1: 1,500-ft^2 house	1115	2.5	0.12	3
Scenario #2: small furnished room	30	3.5	0.05	1

Worst-case scenario

Predicted impacts on indoor air quality (IAQ) (ii/iii)

- **OZONE:**
  - PAC3 in **scenario 2**: $\Delta C = 22 – 191\ \mu g \cdot m^{-3}$, exceeded:
    - ✓ California REL for acute levels ($180\ \mu g \cdot m^{-3}$)
    - ✓ California outdoor air quality standards (1-h: $180\ \mu g \cdot m^{-3}$; 8-h: $140\ \mu g \cdot m^{-3}$)
    - ✓ ARB regulations on air cleaner emissions ($100\ \mu g \cdot m^{-3}$)
  - PAC 3 in **scenario 1**: $\Delta C = 2 – 19\ \mu g \cdot m^{-3}$
  - PAC 4 in **scenario 2**: $\Delta C = 0.6 – 5.5\ \mu g \cdot m^{-3}$

- **FORMALDEHYDE**:
  - PAC1, PAC2 and PAC4 in **scenario 2** increased indoor levels by $\Delta C = 22$, 20 and $17\ \mu g \cdot m^{-3}$ respectively, exceeding California REL for chronic exposure ($9\ \mu g \cdot m^{-3}$)
  - Other three devices removed formaldehyde in similar amounts

Predicted impacts on indoor air quality (IAQ) (iii/iii)

- **BENZENE:**
  - PAC2 and PAC5 in **scenario 2**: ΔC = 9 and 27 $\mu g \cdot m^{-3}$ respectively, exceeded California's Prop 65 levels for inhalation exposure (0.8 and 3 $\mu g \cdot m^{-3}$)
  - The other four devices removed benzene from indoor air

- **UFP**:
  - PAC3 emitted a significant level of UFPs in the presence of ozone-reacting VOCs (limonene, styrene)
  - The **yield** of secondary organic aerosol was **1- 5 %** (consistent with values measured previously for these reactions)

- **ROS:**
  - Higher-than background levels measured directly at the outlet of PAC4

Conclusions and recommendations

- Emissions of pollutants from portable air cleaners were observed, **exceeding California reference levels for three pollutants** in realistic scenarios (ozone, formaldehyde and benzene)
- One device (not certified by ARB) emitted **ozone at potentially harmful levels**, exceeding State and EPA's standards; led to **UFP formation**
- **Standard test procedures are needed** to measure harmful emissions and verify the validity of marketing claims
- VOC removal efficiencies were < 40%. There is a **great opportunity for improving VOC removal performance**
- There is a need for developing and implementing **better engineering controls** to prevent harmful pollutants from being released indoors (e.g., filters/catalysts to remove ozone or ROS downstream of a plasma generator)
- Use of **ozone-generating VUV lamps** should be discouraged

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Questions?